X-ray Reflectivity Study of Organic-Inorganic Electro-Optic Materials with High Refraction Indices

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Introduction: Acentric organic materials integrated into advanced optoelectronic devices promise greatly increased information handling density and reduced device design complexity [1]. Chemisorptive siloxane-based layer-by-layer self-assembly (SA) yields intrinsically acentric chromophore arrays directly on silicon, allowing ready device integration and offering potentially higher electro-optic coefficients and lower dielectric constants than established inorganic materials. Integrating high refraction index inorganic materials in siloxane-based organic superlattices is of interest for preventing insufficient refractive index contrast between organic SA films and device materials and for improving efficiency of future optoelectronic SA-components.

Methods and Materials: We used an all-'wet-chemical' siloxane-based approach for layer-by-layer SA superlattice architecture control by intercalating metal oxide sheets of Ga in an organic noncentrosymmetric multiplayer structure (Fig. 1a). The chromophore deposition and hydroxyl-deprotection steps were characterized previously [2]. In order to determine the thickness and microstructure of the resulting four-component multilayer composition formed with each deposition, specular x-ray reflectivity (XRR) measurements were performed on a series of films deposited onto the native oxide surface of single crystal Si(111) using the identical SA procedure.

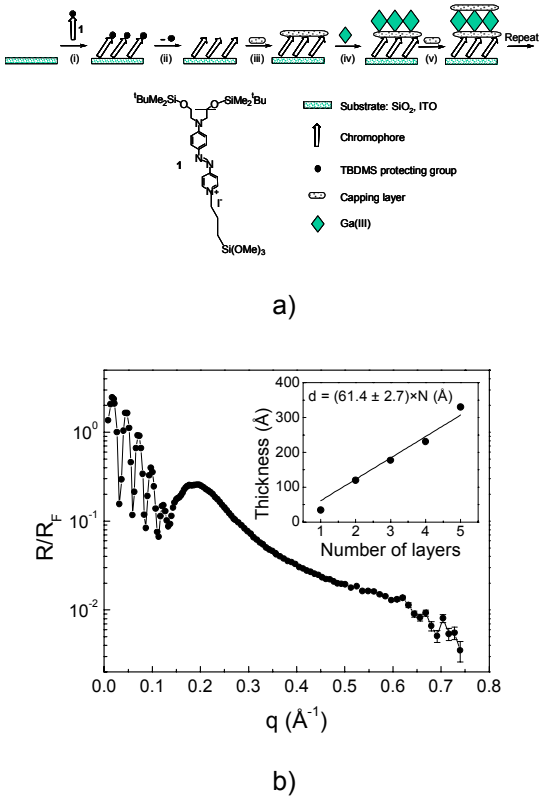

Figure 1. a) Schematic representation of the self-assembly of **1**-based chromophoric hybrid superlattices; b) X-ray reflectivity data for a sample with 4 layers. The inset shows the XRR-derived thicknesses for the SA chromophoric hybrid superlattices as a function of the number of layers.

Results: Typical XRR data normalized to the Fresnel reflectivity for a sample with four successive depositions are shown in Fig. 1b. Fitting of these data to an appropriate structural model provides insight into the microstructural details of the film. The linear dependence of the XRR-derived film thickness on the number of layers (inset of Fig. 1a) demonstrates that equal densities of uniformly oriented chromophores, polysiloxane, and gallium oxide are deposited in each assembled layer. From the slope of the thickness vs. number of layers, an average interlayer spacing of 61.4±2.7 Å is deduced. The chromophore and siloxane layers are 12 and 8 Å, respectively. The electron density of the hybrid film is ~140% that of the native oxide, indicating the presence of a relative dense (inorganic) structure (e.g., compared with all-organic based and Ga_2O_3 films where ρ_{film}/ρ_{Si} ~0.49 [2] and ~2.19, respectively). X-ray diffraction measurements suggest an amorphous film structure.

Conclusions: These observations with a known high-β chromophore and a commercially available gallium precursor demonstrate an efficient 'one-pot' approach to assembling organic-inorganic hybrid EO-superlattices having a high refraction index. This solution-based deposition of metal oxide interfaces is suitable for nanometer range film costruction with vertical organization of different 'sandwich'-type layers and might represent a new entry to modify physico-chemical properties of siloxane-based functional multilayers.

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References: [1] Y. Shi et al, Science **288**, 192 (2000); [2] M.E. van der Boom et al, Polymer Mat. Sci. Eng. **83**, 160 (2000).